Synthesis of Ultraviolet Absorbers Having 2-Hydroxybenzophenone Moiety as the Functional Group

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REVIEW

Synthesis of Ultraviolet Absorbers Having 2-Hydroxybenzophenone Moiety as the Functional Group

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This article involves the synthetic methods of ultraviolet absorbers having 2-hydroxybenzophenone moiety as the functional group.

KEY WORDS: Ultraviolet Absorber/ 2,4-Dihydroxybenzophenone/ 4-Alkoxy-2-hydroxybenzophenone/ 2,2′,4,4′-Tetrahydroxybenzophenone/ 2,2′-Dihydroxy-4,4′-dimethoxybenzophenone/ 2,4,4′-Trihydroxybenzophenone/ 2,4-Dihydroxy-4′-methoxybenzophenone/ 2,2′,4-Trihydroxybenzophenone/

I. INTRODUCTION

The ultraviolet absorbers having 2-hydroxybenzophenone moiety as the functional group are known commonly as those of 2-hydroxybenzophenone type. It has been proposed[1] that, when ultraviolet was irradiated, the proton of their 2-hydroxy group transfers to the oxygen of carbonyl group affording the excited quinoid form and it can migrate back again to provide the former phenolic structure under giving out heat, fluorescence, or phosphorescence (Scheme 1). This is the main function of the ultraviolet absorbers of 2-hydroxybenzophenone type. However, it has been proposed[2] lately that they also function in decomposing alkyl peroxide into alkoxy radical as well as in preventing the chain reaction of generated alkoxy radical by imparting a hydrogen radical to it (Scheme 1). The ultraviolet absorbers of 2-hydroxybenzophenone type are used for the improvement of light fastness of polymers and the other components. Such the lightfastness has been improved often by the synergistic effect when they were used together with one or more of hindered phenols, hindered amines, sulfur compounds, and phosphorous compounds. The most parts of well-known ultraviolet absorbers of 2-hydroxybenzophenone type are polyhydroxybenzophenones such as 2,4-dihydroxy-, 2,2′,4,4′-tetrahydroxy-, 2,4,4′-trihydroxy-, and 2,2′,4-trihydroxybenzophenone as well as their derivatives. Especially, the derivatives lastly described are desirable as the practical ultraviolet absorbers, because such the derivatives are less volatile and more susceptible to polymers and the other components compared to the polyhydroxybenzophenones themselves.

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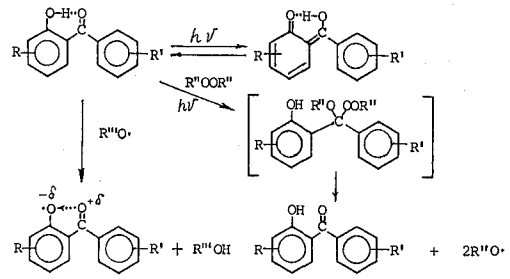
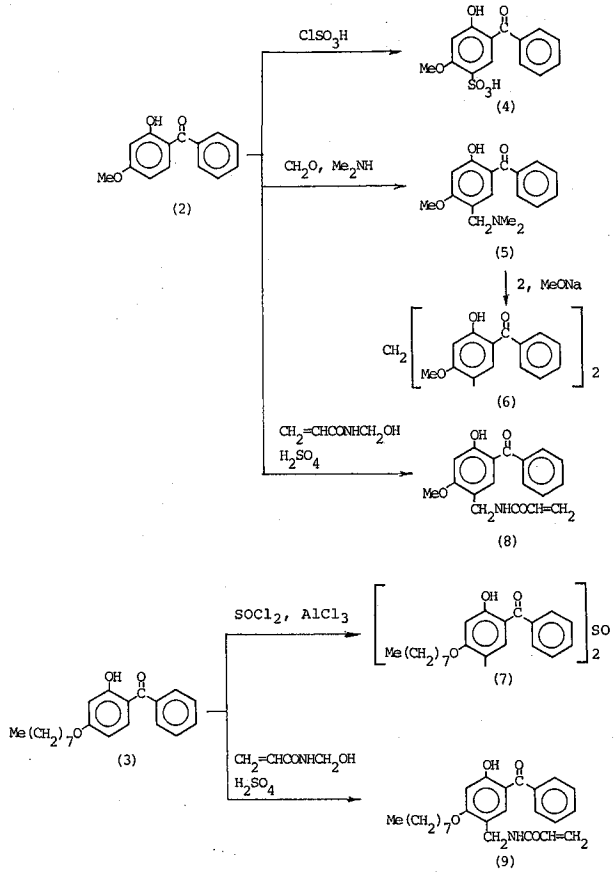


Scheme 1

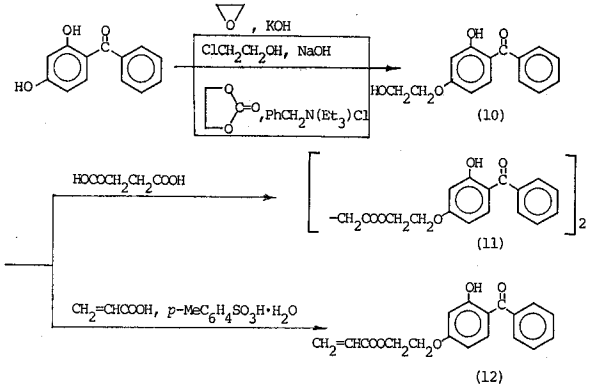
II. PREPARATIONS AND CHEMICAL MODIFICATIONS OF 2,4-DIHYDROXYBENZOPHENONE AND 4-ALKOXY-2-HYDROXYBENZOPHENONES

It is well-known that 2,4-dihydroxybenzophenone (**1**) is synthesized by Friedel-Crafts acylation of resorcinol with benzoyl chloride in the presence of $AlCl_3$ or by adding benzotrichloride to a solution of resorcinol in aqueous methanol followed by heating. Though the compound **1** itself is employed sometimes, some of its derivatives are used more frequently as the practical ultraviolet absorbers. When a solution of **1** in aqueous NaOH is



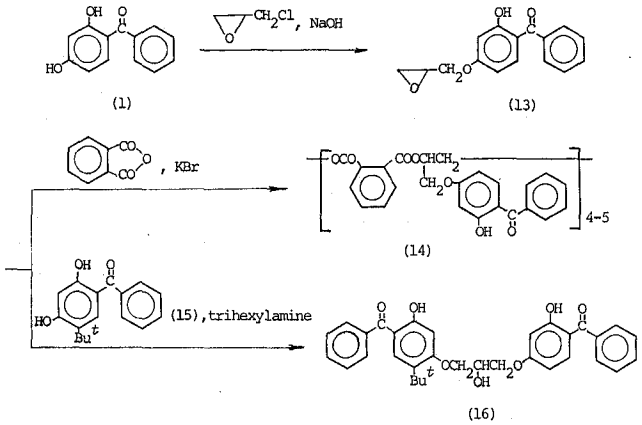
(561)

treated with dimethylsulfate, 2-hydroxy-4-methoxybenzophenone (**2**) is produced.[3] Also, when **1** is allowed to react with octyl chloride or bromide in the presence of a surfactant in refluxing aqueous KOH, 2-hydroxy-4-(octyloxy)benzophenone (**3**) is produced.[4] The compound **2** in ethyl acetate is treated with $ClSO_3H$ at 0–5°C and then stirred overnight at room temperature to afford 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (**4**).[5] Also, the compound **2** in methanol is refluxed together with a slight excess of aqueous dimethylamine and 37% aqueous formaldehyde affording 5-[(dimethylamino)methyl]-2-hydroxy-4-methoxybenzophenone (**5**).[6] The obtained compound **5** is further allowed to condense with **2** in the presence of a small amount of Na methoxide in butyl alcohol under heating to afford 5,5′-methylenebis(2-hydroxy-4-methoxybenzophenone) (**6**).[6] The compound **3** is treated with $SOCl_2$ and $AlCl_3$ affording 5,5′-sulfinylbis[2-hydroxy-4-(octyloxy)benzophenone] (**7**).[7] Both **2** and **3** are converted to polymerizable ultraviolet absorbers, **8** and **9**, respectively, by the reaction with *N*-(hydroxymethyl)acrylamide in 95% H_2SO_4 at low temperature.[8] 2-Hydroxy-4-(2-hydroxyethoxy)benzophenone (**10**) is synthesized[9] by the procedure which involves the following operations; heating a mixture of wet **1**, a small amount of 45% aqueous KOH, and an adequate amount of H_2O under nitrogen (nearly 0.2 atmosphere) in an autoclave at 105–110°C, introduction of nitrogen into the autoclave until a pressure of 2–3 atomospheres is reached, and feeding an appropriate amount of ethylene oxide at a proper pumping speed keeping the pressure inside the autoclave below 6 atmospheres followed by shaking the autoclave. Also, the compound **10** is synthesized by treating **1** with ethylene chlorohydrin in the presence of NaOH (0.5–1.2 molar equivalents based on **1**) at 70°C for 18 h[10] or with ethylene carbonate in the presence of benzyltriethylammonium chloride at 140–150°C for 11 h followed by addition of H_2O to the reaction mixture at 100°C.[11] It is allowed to condense with a few dicarboxylic acids

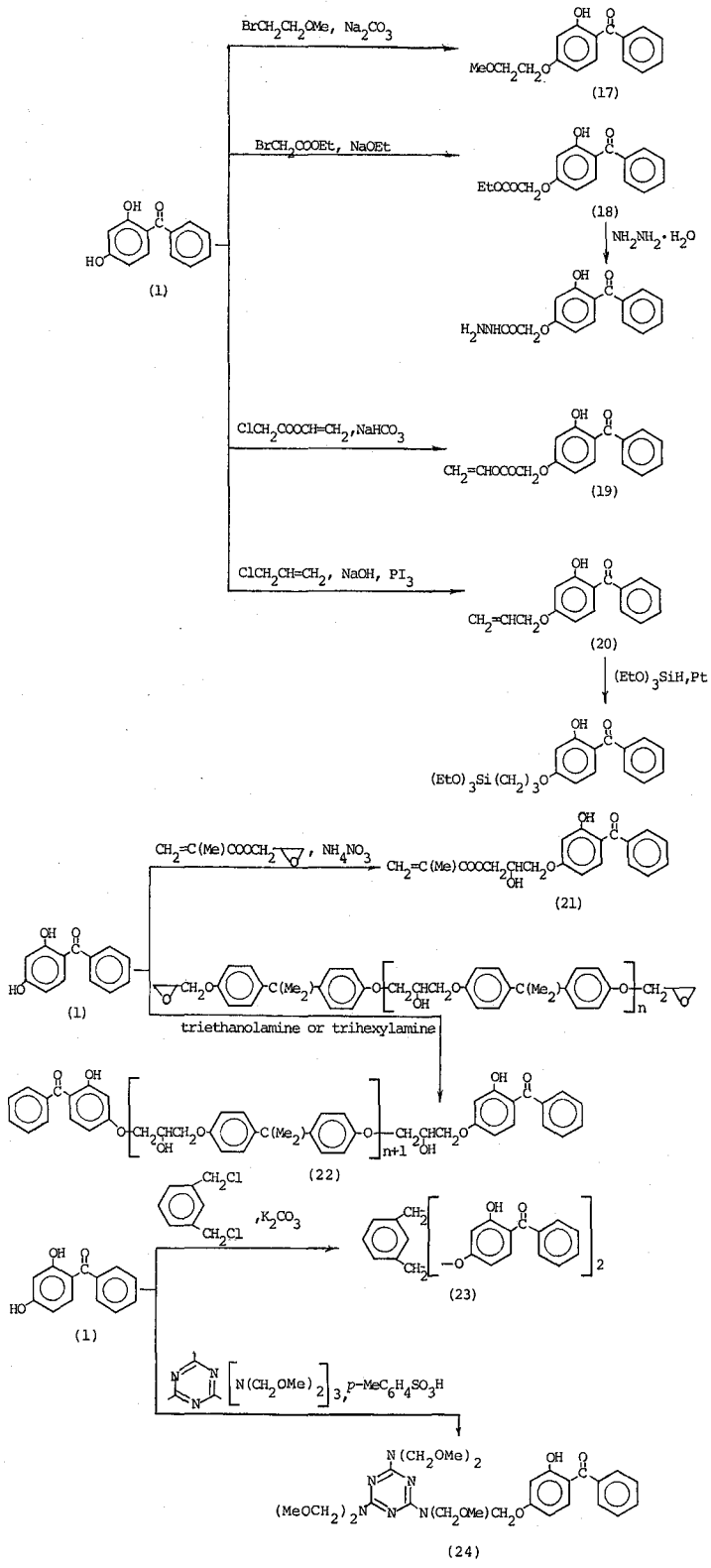


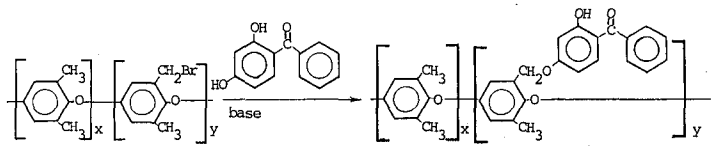
affording ultraviolet absorbers of low volatility. For example, a mixture of **10** and a half molar equivalent of succinic acid is heated at 200–210°C with removal of the H_2O formed to afford **11**.[12] And, when **10** is allowed to react with acrylic acid in boiling benzene containing *p*-toluenesulfonic acid monohydrate and hydroquinone in small amounts under nitrogen while the H_2O formed is removed, a polymerizable ultraviolet absorber **12** is obtained.[13] 4-(2,3-Epoxypropoxy)-2-hydroxybenzophenone (**13**), which seems to be a reactive ultraviolet absorber, is prepared by allowing **1** to react with an excess of epichloro-

hydrin in H_2O containing NaOH (0.4–0.5 molar equivalent based on **1**) at 60°C.[14] When **13** is allowed to react with phthalic anhydride in the presence of a small amount of KBr under nitrogen in an enclosed vessel at 110°C, a polyester, which is represented by the formula numbered with **14**, is produced.[15] Also, when a solution of **13**, 5-*tert*-butyl-2,4-dihydroxybenzophenone (**15**), and trihexylamine as a catalyst in xylenes is heated at 125°C,



16 is produced.[16] In this case, the employed **15** has been synthesized by the reaction of **1** with isobutylene in the presence of 10% tetraphosphoric acid/bleaching earth in nitrobenzene at 120°C.[17] The compound **17**, **18**, **19**, and **20** are also found in the literature. All of them, except for **17**, seem to be reactive ultraviolet absorbers. The compound **17** is synthesized by allowing **1** to react with 2-bromoethyl methyl ether in acetone in the presence of Na_2CO_3 at 50–55°C under stirring.[18] The compound **18** is synthesized by heating **1** in ethanolic sodium ethoxide with ethyl bromoacetate.[19] It is derived to the corresponding hydrazide by the condensation using 85% hydrazine monohydrate in isopropyl alcohol at room temperature.[20] The compound **19**, which is proposed as a reactive ultraviolet stabilizer in the literature, is synthesized by stirring a mixture of **1**, vinyl chloroacetate, $NaHCO_3$, and a small amount of methyl-1,4-benzoquinone in acetonitrile at 80°C.[21] And, the last compound **20** is synthesized by the dehydrohalogenation between **1** and allyl chloride or bromide in the presence of NaOH and a small amount of PI_3 in diethylene glycol at 175°C.[22] It is hydrosilylated with triethoxysilane in the presence of Pt in toluene affording a silicon-containing ultraviolet stabilizer of 2-hydroxybenzophenone type.[23] The reaction of **1** with glycidyl methacrylate in the presence of a small amount of NH_4NO_3 at 80°C under nitrogen provides a polymerizable ultraviolet absorber **21**.[24] Also, the reaction of **1** with an epoxy resin of bisphenol type (n is not given) in the presence of triethanolamine or trihexylamine at 130°C under nitrogen provides a polymeric ultraviolet absorber **22**.[25] Besides, the compounds **23**, **24**, and **25** are found in the literature. The compound **23** is synthesized by the condensation of **1** with α,α'-dichloro-*m*-xylene in the presence of K_2CO_3 in boiling cyclohexanone.[26] The compound **24** is synthesized by treating **1** with *N,N,N'N',N'',N''*-hexakis(methoxymethyl)-1,3,5-triazine-2,4,6-triamine in xylenes in the pres-



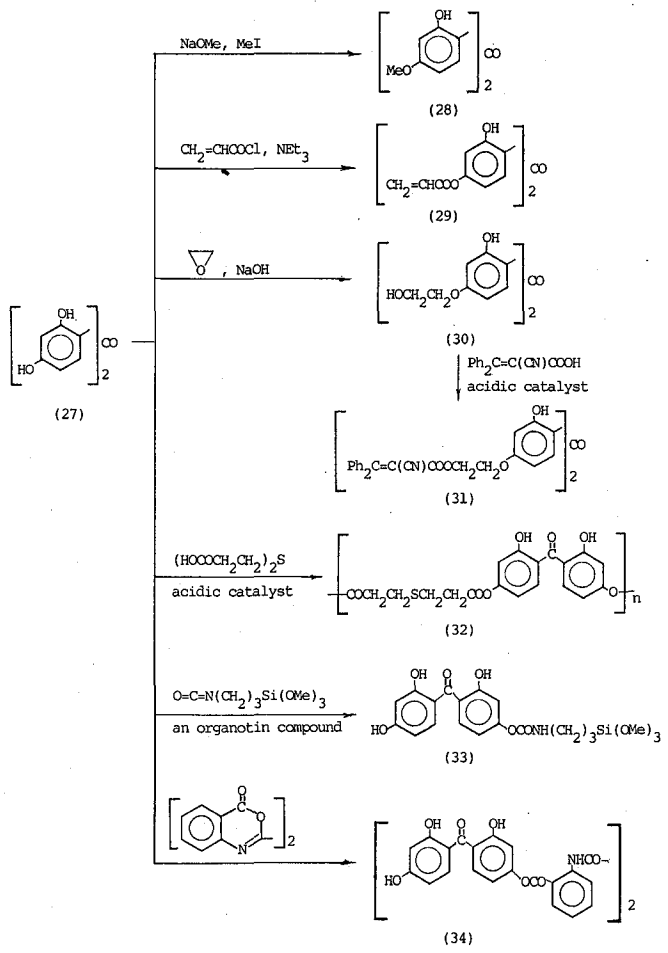


(26) (25)

ence of *p*-toluenesulfonic acid at 120°C.[27] And, the compound **25**, which is proposed as an excellent polymeric light stabilizer in the literature, is synthesized by treating a partially brominated poly[oxy(2,6-dimethyl-1,4-phenylene)] (**26**) with **1** under alkaline conditions.[28] In this case, the employed **26** has been prepared by the reaction of poly[oxy(2,6-dimethyl-1,4-phenylene)] with *N*-bromosuccinimide in an appropriate medium.

III. PREPARATIONS AND CHEMICAL MODIFICATIONS OF 2,2′,4,4′-TETRAHYDROXYBENZOPHENONE AND 2,2′-DIHYDROXY-4,4′-DIMETHOXYBENZOPHENONE

When a mixture of 2,4-dihydroxybenzoic acid, resorcinol, and a relatively large amount of $ZnCl_2$ as well as $POCl_3$ is heated at 80–90°C under stirring, 2,2′,4,4′-tetrahydroxybenzophenone (**27**) is produced.[29] Two alternative methods for preparing **27** are found in the literature. Thus, resorcinol is treated with phosgene in the presence of $ZrCl_4$ in nitrobenzene at 70°C giving **27**.[30] Also, 3-hydroxyphenyl 2,4-dihydroxybenzoate is heated in the presence of $ZrCl_4$ in nitrobenzene at 70°C to give **27**.[31] Several publications which describe the usefulness of **27** as light stabilizer are found in the literature.[32] Also, a patent literature claims that a sinergistic effect has been observed when **27** was used together with 2,4-dimethyl-6-isobornylphenol which is a hindered phenolic light stabilizer.[33] Among the derivatives of **27**, 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (**28**) is most frequently used as light stabilizer. It can be synthesized by methylating the tetrasodium salt of **27** with two molar equivalents of methyl iodide in the presence of sodium methoxide in methanol.[34] It can also be enythesized [34] by the procedure which involves the following operations; addition of $AlCl_3$ to a cold (0°C) solution of 1,3-dimethoxybenzene in 1,2-dichloroethane, bubbling of phosgene through the reaction mixture maintained at 0–4°C (for 1.5 h), 10°C (for 1 h), and then 16°C (for 3 h), stirring the reaction mixture at room temperature overnight without the bubbling of phosgene, and decomposing the reaction mixture maintained at 40–50°C with ice-water. The reaction of **27** with acryloyl chloride in the presence of triethylamine in dichloromethane provides **29** which is a crosslinking ultraviolet absorber.[35] The reaction of **27** with ethylene oxide in hot (55°C) water containing a small amount of NaOH followed by neutralization with dilute hydrochloric acid provides **30**.[36] The compound **30** is further converted to **31** by ester condensation with 2-cyano-3,3-diphenylacrylic acid in the presence of a proper acidic catalyst.[37] Polycondensation of **37** with 3,3′-thiodipropionic acid under the proper conditions provides a polymeric ultraviolet absorber (**32**, n is not apparent) of less extractability.[38] When **27** in *N,N*-dimethylformamide is heated together with γ-isocyanatopropyltrimethoxysilane under the catalytic action of an organotin compound, a silicon-containing ultraviolet absorber of 2-hydroxybenzophenone

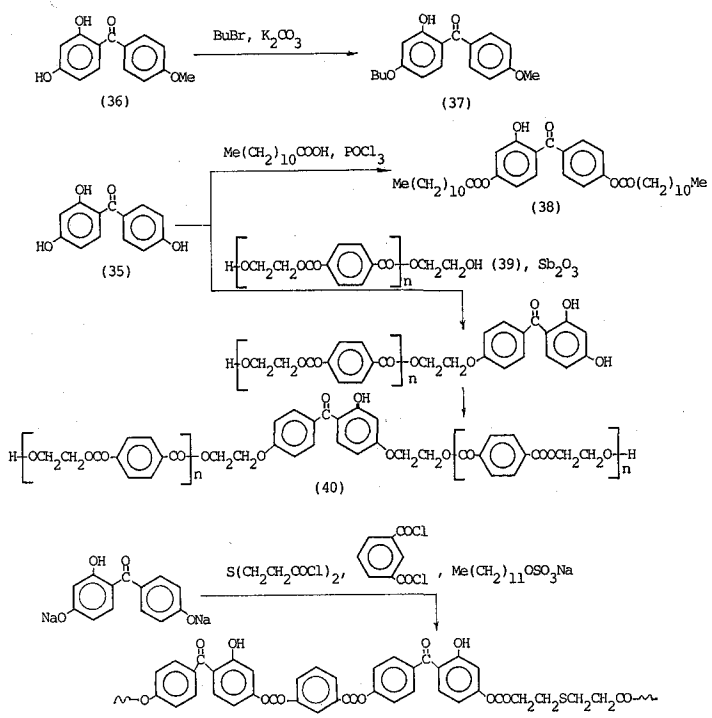


type (**33**) is obtained.[39] Also, when a mixture of **27** and [2,2′-bi-4*H*-3,1-benzoxazine]-4,4′-dione is heated at 240°C, the compound **34** of symmetrical structure is obtained.[40]

IV. PREPARATIONS AND CHEMICAL MODIFICATIONS OF 2,4,4′-TRIHYDROXYBENZOPHENONE AND 2,4-DIHYDROXY-4′-METHOXYBENZOPHENONE

2,4,4′-Trihydroxybenzophenone (**35**) is synthesized by adding a half molar equivalent (based on resorcinol) of gaseous BF_3 to a solution of 4-hydroxybenzoic acid and resorcinol in 1,1,2,2-tetrachloroethane followed by heating on a steam bath.[41] It is also synthesized by the treatment of a hot (40°C) mixture of 4-hydroxybenzoic acid, resorcinol, and relatively large amounts of $ZnCl_2$ and about 100% H_3PO_4 with PCl_3 followed by stirring the mixture at 60°C.[42] When 4-methoxybenzoic acid is used instead of 4-hydroxybenzoic acid in the above reaction, the analogous condensation between 4-methoxybenzoic acid and resorcinol takes place affording 2,4-dihydroxy-4′-methoxybenzophenone (**36**).[42] The compound **36** is allowed to condense with bromobutane in the presence of K_2CO_3 to afford 4-butoxy-2-

hydroxy-4′-methoxybenzophenone (**37**).[43] The compound **35** is converted to 4,4′-diacyloxy-2-hydroxybenzophenones by the condensations using several C_{6-18} even-numbered fatty acids and $POCl_3$ as a condensing agent. For example, 4,4′-dilauroyloxy-2-hydroxybenzophenone (**38**) is prepared by heating a mixture of **35**, two molar equivalents of lauric acid, and $POCl_3$ at 120–130°C.[44] When a mixture of conventional precursor (**39**, n is not given) for preparation of poly(ethylene terephthalate) and **35** (weight ratio is 100 : 0.91) is heated together with a catalytic amount of Sb_2O_3 at 230–290°C while the pressure in reaction vessel is reduced slowly to 3 millibar with removal of the low-boiling substances such as

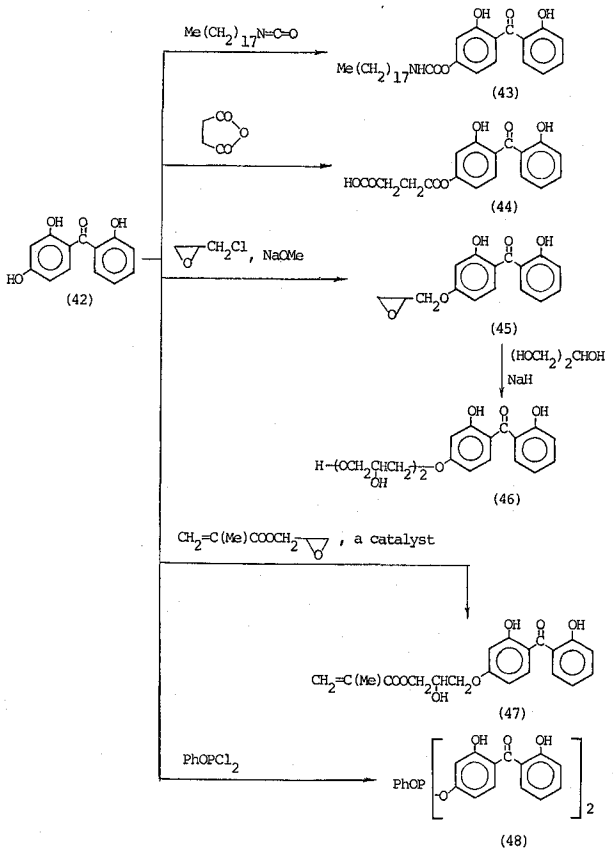


ethylene glycol by distillation, a polymeric ultraviolet absorber **40** is produced.[45] Also, when a finely dispersed mixture of the disodium salt of **35** and sodium lauryl sulfate is quickly mixed with a solution of 3,3′-thiodipropionyl chloride and isophthaloyl dichloride in chloroform followed by vigorous agitation at room temperature, a polymeric ultraviolet absorber, which is represented by the formula numbered with **41**, is produced.[46]

V. PREPARATION AND CHEMICAL MODIFICATION OF 2,2′,4-TRIHYDROXYBENZOPHENONE

2,2′,4-Trimethoxybenzophenone, which is a precursor of 2,2′,4-trihydroxybenzophenone (**42**), is synthesized by the procedure which involves the following operations; the first heating of a mixture of 2-methoxybenzoyl chloride and a relatively large amount of 1,3-

dimethoxybenzene in order to start the reaction between these two compounds, removement of the heat source when an vigorous reaction occurred, and the second heating of the reaction mixture after the vigorous reaction subsided in order to remove all of the hydrogen chloride generated. 2,2′,4-Trimethoxybenzophenone thus obtained is dissolved in 1,2-dichloroethane and allowed to react with a large amount of $AlCl_3$ at 100°C followed by decomposition with dilute hydrochloric acid to afford **42**.[47] The compound **42** is used as a ultraviolet absorber in a few cases. When **42** is allowed to react with octadecyl isocyanate, the compound **43**, which improves the lightfastness of polyurethane elastomers, is produced.[48] When **42** in dry picoline is mixed slowly with succinic anhydride at < 60°C and the mixture is heated at 60°C, the compound **44** is produced.[49] When a mixture of **42** and one molar equivalent of epichlorohydrin is treated dropwise with a solution of one molar equivalent of Na methoxide in methanol at 60–65°C, 2,2′-dihydroxy-4-(2,3-epoxypropoxy)benzophenone (**45**) is produced.[50] Further, the compound **45** is heated together with a large amount of glycerol under the catalytic action of NaH at 100°C to afford **46**.[50] Besides, the compounds **47** and **48** are found in the literature. The former, which is a polymerizable ultraviolet absorber, is synthesized by allowing **42** to react with glycidyl methacrylate in the presence of an appropriate catalyst.[51] The latter is synthesized by the treatment of **42** with phosphorodichloridous acid phenyl ester in benzene.[52]



VI. SUMMARY

This article does not cover all of the compounds which belong to the ultraviolet absorbers of 2-hydroxybenzophenone type. Several or more of such compounds as those having Cl, methyl group, or the both on the benzene rings of their 2-hydroxybenzophenone moieties are omitted, because they seem to belong to the minor classes of the ultraviolet absorbers above-mentioned and are not so often found in the literature. Thus, this article will cover the most parts of ultraviolet absorbers of this type. Especially, the compounds **1**, **2**, **3**, **6** and **28** described in this article are put in the market.

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